RIXS and excited states calculation with the Xclaim code

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We describe the calculation of resonant inelastic x-ray scattering (RIXS) with Xclaim (a multi-plaform code for the calculation of core-hole spectroscopy based on a ligand-field multiplet model). RIXS can be calcuated with a crystal-field and charge transfer model with ligands for the $M_{2,3}$, $L_{2,3}$, and K_α K_β edges for d-valence metals. In addition, we describe the full diagonalization of the hamiltonian to classify the excited states. The command line use of xclaim is described for scripting purposes to help in automatizing and reproducing the results that can be obtained with the graphical interface.

Resonant inelastic x-ray scattering (RIXS) is an experimental technique for observing different types of excitations (dd, charge transfer, magnons, etc.) that has attracted a lot of interest. [1, 2] Amongst its advantages can be cited chemical and bulk selectivity, and the possibility to be used at high pressure. However, multiplet effects can make its interpretation not straightforward. A many-body model is necessary many times to take into account the character of the electronic structure of strongly correlated materials, and the interaction with the core hole in the final states.

Xclaim [3, 4] is a code for the calculation of core-hole spectroscopy using a ligand-field multiplet model [5, 6]. The hamiltonian matrices and spectroscopy is calculated by a compiled fortran code with the input parameters being set in an interface in python. The input parameters can be set in the main window of the graphical interface (Fig. 1). In this paper we descibe the extension of the code for calculating RIXS and classifying the excited states. We also discuss the use of xclaim as a command line tool, that allows to reliably reproduce previous calculations and automatize the process of calculating spectra.

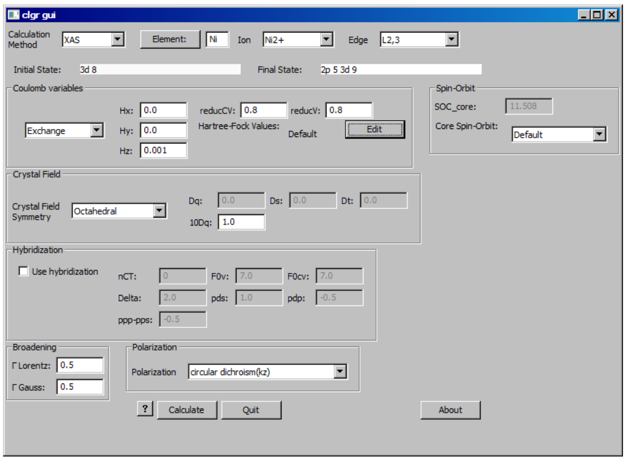


FIG. 1: Main input window for xclaim. Atomic, crystal field, and charge transfer parameters for the calculation can be set in the input boxes. Pop-up windows can be used for the detailed modification of Coulomb and spin-orbit parameters, and the use of a general crystal-field in terms of Wybourne parameters.

1. RIXS CALCULATION

A common scattering geometry is to use 90^o between incident and scatterd beam to minimize the elastic scattering, and to use σ and π polarization for the incoming light. No polarization analysis is normally used for the outgoing beam, since it would atenuate too much the beam.

The RIXS calculation done by full diagonalizations of the hamiltonian matrices can be subdivided into several independent processes. Each diagonalization can be separated into two independent processes for the upper and lower eigenvalues (in the case of K_α and K_β RIXS three hamiltonian matrices need to be diagonalized). The lorrentzian and gaussian convolutions of the RIXS map are also paralellized. The usage of the multiprocessing python library allows to launch several independent python processes from the python interpreter and doing the calculation in a computer with several processor cores will notably speed up the RIXS calculation.

2. EXCITED STATES

In addition to ground state expectation values it is possible to also characterize the excited states from an exact diagonalization of the hamiltonian. By selecting *diagonalize* in the spectroscopy tab the program will calculate the hamiltonian, fully diagonalize it and show a text window with the energy positioning and information for the excited states (Fig. 3). The text window shows for each quantum state the energy positioning E, the number of valence electrons, x, y and z components of the orbital angular momentum $\mathbf{L}$ and spin $\mathbf{S}$, the expected value of the spin orbit for each state (labeled by $L.S$), the total spin $\hat{\mathbf{S}}^2 = S(S+1)$ (this is related to the spin multiplicity, i.e. singlet, doublet...), and the occupation of the different d orbitals: d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{yz}, and d_{zx}. In

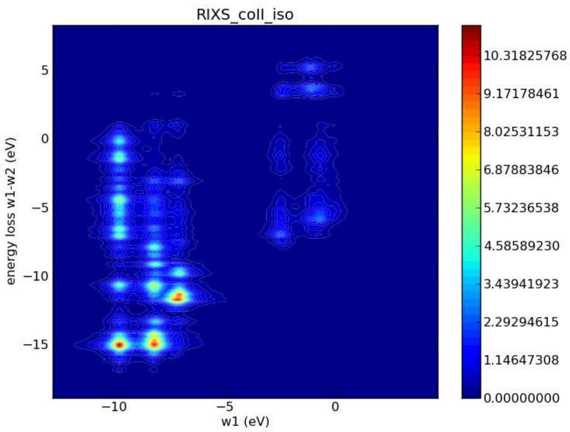


FIG. 2: Output contour plot for a RIXS calculation for Co^{2+} at the K_α
edge based on a crystal field model (ref. [7]).

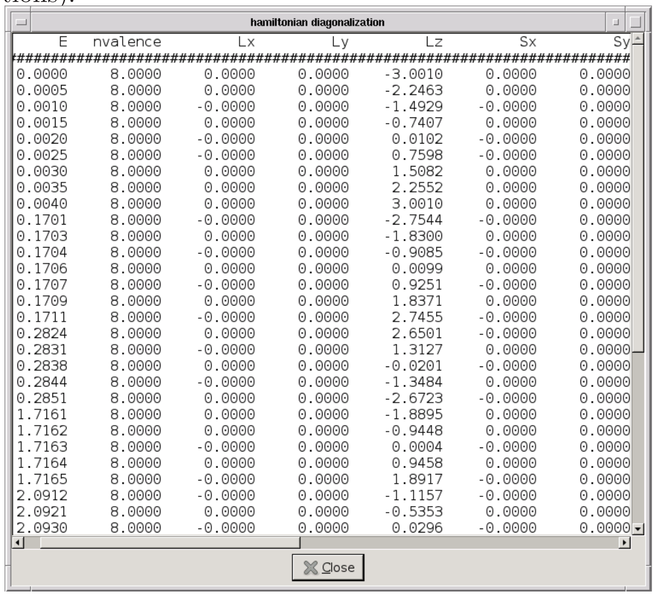
the case of a calculation with ligands it will output the occupation of the valence and ligand shells.

Information on excitations can be used in the interpretation of RIXS spectra. or pump-probe experiments, where the system undergoes a cascading decay through excited quantum states. [8, 9]. Another interest for studying excitations comes from finding systems where crystal-field exctiations very close to the ground state allow to easily switch the ground state, and therefore change dramatically the physical properties of the system, by small changes in the ligand environment. [10]

- The information shown on Crystal-field (dd) and charge-transfer excitations
- transition-metal complex

3. COMMAND LINE INTERFACE

In addition to using the graphical interface, it is possible to run the program from the command-line and to repeat the calculation with the same parameters as set previously on the graphical interface, or modifying them. The file *out/input.txt* contains the parameters saved from the last execution of the program. Note that *out/input.txt* is rewritten each time the *Calculate* button is pressed or when the command line interface is run. The input file is saved as a python dictionary, between braces and different lines formated as *"label": value,* pairs. Values can be numerical or a string given between quotes. The *out* directory also contains other files depending on the type of calculation that is run: *GS_info.txt* (calculated expectation values for the ground state) and the files *poles_.txt* (calulated spectra for different polarizations).



hamiltonian diagonalization

E	nvalence	Lx	Ly	Lz	Sx	Sy
0.0000	8.0000	0.0000	0.0000	-3.0010	0.0000	0.0000
0.0005	8.0000	0.0000	0.0000	-2.2463	0.0000	0.0000
0.0010	8.0000	-0.0000	0.0000	-1.4929	-0.0000	0.0000
0.0015	8.0000	0.0000	0.0000	-0.7407	0.0000	0.0000
0.0020	8.0000	-0.0000	0.0000	0.0102	-0.0000	0.0000
0.0025	8.0000	-0.0000	0.0000	0.7598	-0.0000	0.0000
0.0030	8.0000	0.0000	0.0000	1.5082	0.0000	0.0000
0.0035	8.0000	0.0000	0.0000	2.2552	0.0000	0.0000
0.0040	8.0000	0.0000	0.0000	3.0010	0.0000	0.0000
0.1701	8.0000	-0.0000	0.0000	-2.7544	-0.0000	0.0000
0.1703	8.0000	0.0000	0.0000	-1.8300	0.0000	0.0000
0.1704	8.0000	-0.0000	0.0000	-0.9085	-0.0000	0.0000
0.1706	8.0000	0.0000	0.0000	0.0099	0.0000	0.0000
0.1707	8.0000	-0.0000	0.0000	0.9251	-0.0000	0.0000
0.1709	8.0000	0.0000	0.0000	1.8371	0.0000	0.0000
0.1711	8.0000	-0.0000	0.0000	2.7455	-0.0000	0.0000
0.2824	8.0000	0.0000	0.0000	2.6501	-0.0000	0.0000
0.2831	8.0000	-0.0000	0.0000	1.3127	0.0000	0.0000
0.2838	8.0000	0.0000	0.0000	-0.0201	-0.0000	0.0000
0.2844	8.0000	-0.0000	0.0000	-1.3484	0.0000	0.0000
0.2851	8.0000	0.0000	0.0000	-2.6723	-0.0000	0.0000
1.7161	8.0000	0.0000	0.0000	-1.8895	0.0000	0.0000
1.7162	8.0000	0.0000	0.0000	-0.9448	0.0000	0.0000
1.7163	8.0000	-0.0000	0.0000	0.0004	-0.0000	0.0000
1.7164	8.0000	0.0000	0.0000	0.9458	0.0000	0.0000
1.7165	8.0000	-0.0000	0.0000	1.8917	-0.0000	0.0000
2.0912	8.0000	-0.0000	0.0000	-1.1157	-0.0000	0.0000
2.0921	8.0000	0.0000	0.0000	-0.5353	0.0000	0.0000
2.0930	8.0000	-0.0000	0.0000	0.0296	-0.0000	0.0000

Close

FIG. 3: Window showing the results of diagonalizing the hamiltonian.

To use the comand line interface just type *cp out/input.txt input1.txt ./xclaim_gui.py -i input1.txt* The resulting spectra and ground state expectation values will be in the directory *out* (its contents will be overwritten). A complete list of options can be seen by typing *./xclaim_gui.py –help* The xclaim webpage [3] contains more detailed information about the command line and rebroadening spectra.

4. ACKNOWLEDGEMENTS

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